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## Steady Shear Compliance of Concentrated Polystyrene Solutions

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The complex modulus and the normal and shear stresses in steady shear flow were measured on concentrated solutions of polystyrene in toluene, dioctyl phthalate and chlorinated diphenyl. The range of concentration was 7 to 30 g/dl and that of molecular weight  $3.3 \times 10^4$  to  $2.5 \times 10^6$ , respectively. The polystyrene samples were of thermally polymerized type but one sample of the living type with a sharp distribution of molecular weight. The steady shear compliance  $J_e$  was evaluated either from the complex modulus or from the normal stress and the shear stress. The result showed that  $J_e$  was independent of the molecular weight and was inversely proportional to the second power of the concentration in solutions of high molecular-weight polystyrenes.  $J_e$  of the living polystyrene sample was much smaller than that of thermal polystyrene. Empirical formula for  $J_e$  of high molecular-weight polystyrene in solutions were obtained as

$$\begin{aligned} J_e &= 6 \times 10^{-6} c^{-2} \quad (\text{thermal polystyrene}) \\ &= 3 \times 10^{-6} c^{-2} \quad (\text{living polystyrene}). \end{aligned}$$

Here  $J_e$  is expressed in unit of  $\text{dyne}^{-1} \cdot \text{cm}^2$  and  $c$  in unit of g/ml. These results were in conflict with the modified Rouse theory but were in agreement with the Hayashi theory. In solutions of low molecular-weight polystyrene,  $J_e$  increased slightly with increasing molecular weight and was inversely proportional to the concentration. This result was not compatible with any existing theory.

### INTRODUCTION

Mechanical properties of polymer solutions at low rate of deformation can be described in terms of two quantities, the viscosity  $\eta$  and steady shear compliance  $J_e$ . The viscosity behavior has been repeatedly investigated with wide variations of polymer species, molecular weight and concentration. It is now widely recognized that the viscosity of concentrated polymer solution is proportional to the 3.4th power of molecular weight  $M$  if  $M$  exceeds a critical value  $M_c$  and to the roughly first power of  $M$  if  $M < M_c^{1,2)}$ . The critical molecular weight  $M_c$  is inversely proportional to the concentration for many polymer systems, and for example, we have

$$cM_c \doteq 4 \times 10^4 \quad (1)$$

in the case of polystyrene solutions. Here the concentration  $c$  is expressed in the unit of g/ml. The rapid increase of  $\eta$  with increasing  $M$  in the range of  $M > M_c$

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is believed attributable to the interchain entanglement of polymer molecules, and the critical molecular weight is interpreted as the molecular weight at which one molecule has one entanglement point on average.

Contrary to the case of the viscosity behavior, there are few systematic data on the steady shear compliance of concentrated polymer solutions. Ferry *et al.* found that  $J_e$  was proportional to  $M/c$  in such a highly concentrated polymer solution as 45-100 % solutions of polyvinyl acetate in diethyl phthalate<sup>39</sup> and 70-100 % solutions of polyisobutylene in cetane<sup>49</sup>. On the other hand, Tobolsky *et al.*<sup>59</sup>, and Odani *et al.*<sup>69</sup>, found that  $J_e$  is primarily independent of the molecular weight in bulk polystyrene and poly- $\alpha$ -methylstyrene, respectively.

Dependence of  $J_e$  on  $M$  or  $c$  can be used as a criterion for the test of theories on the rheological behavior of chain entanglements. The existing theories are conveniently classified into two types. In the first type, the entanglement coupling is assumed to cause, in the chain motion, the viscous friction in excess of that due to the solvent viscosity. This assumption leads to a group of theories such as the modified Rouse theory<sup>79</sup> or the ladder-network theory of Marvin<sup>89</sup>. These theories predict for monodisperse polymers that

$$J_e = (2/5)(M/cRT) \quad (2)$$

where  $R$  is the gas constant and  $T$  is the absolute temperature. On the other hand, in the second type of theories, the entanglement coupling is assumed to give rise to the interaction of elastic nature between non-bonded polymer segments. This assumption leads to the Hayashi theory<sup>99</sup> which predicts that

$$J_e = (3.5/2)(M_e/cRT) \quad (3a)$$

Here  $M_e$  is the so-called "entanglement spacing" and is related to the ordinary critical molecular weight  $M_c$  as

$$M_e = M_c/1.52 \quad (4)$$

Hence, we have

$$J_e = (3.5/3.04)(M_e/cRT) \quad (3b)$$

Combination of Eq. (3b) with Eq. (1) indicates that  $J_e$  is independent of  $M$  and is inversely proportional to  $c^2$ .

Here we report the results of steady shear compliance measurements obtained for concentrated polystyrene solutions. The ranges of molecular weight and concentration covered in this investigation were  $3.3 \times 10^4 \leq M \leq 2.5 \times 10^6$  and  $7 \times 10^{-2} \leq c \leq 3 \times 10^{-1}$  (g/ml), respectively. These ranges include two regions of molecular weight, *i.e.* the region of  $M < M_c$  and of  $M > M_c$ , if  $M_c$  is determined by Eq. (1).

## EXPERIMENTAL

### Method

The steady shear compliance  $J_e$  can be evaluated either from the real and imaginary parts of the complex modulus,  $G'$  and  $G''$ , or from the normal and shear stresses in the steady shear flow,  $\sigma_{ii}$  and  $\sigma_{ij}$ :<sup>109</sup>

$$J_e = \lim_{\omega \rightarrow 0} G'/G''^2 \quad (5a)$$

$$= \lim_{\kappa \rightarrow 0} (\sigma_{11} - \sigma_{22})/2\sigma_{12}^2. \quad (5b)$$

Here  $\omega$  is the angular frequency and  $\kappa$  is the rate of shear. The stress components  $\sigma_{ij}$ 's refer to a cartesian coordinate where 1 indicates the direction of flow, 2 indicates the direction normal to the shear plane and 3 indicates the direction perpendicular to 2 and 3. Thus,  $(\sigma_{11}-\sigma_{22})$  is the primary normal stress and  $\sigma_{12}$  is the shear stress.

The real and imaginary parts of the complex modulus and the shear stress were measured with a coaxial cylinder rheometer, and the normal stress was measured with a parallel plate rheogoniometer. Details of the apparatuses were described previously<sup>11</sup>. The quantity measurable by the parallel plate rheogoniometer is the normal pressure gradient across the diameter,  $\partial P/\partial \ln r$ , which is related to the primary and secondary normal stresses,  $(\sigma_{11}-\sigma_{22})$  and  $(\sigma_{22}-\sigma_{33})$ , as

$$-\frac{\partial P}{\partial \ln r} = \sigma_{11}-\sigma_{22} + (1 + \frac{d}{d \ln \kappa})(\sigma_{22}-\sigma_{33}) \quad (6)$$

As indicated earlier, the second term on the right-hand side of Eq. (6) is, in most cases of polymer solutions including polystyrene solutions<sup>12</sup>, negligibly small compared to the first term at small rate of shear. Therefore,  $(-\partial P/\partial \ln r)$  can be used in Eq. (5) in place of the primary normal stress  $(\sigma_{11}-\sigma_{22})$ . For estimation of  $J_e$  of the systems treated in this study, equation (5b) is more adequate than Eq. (5a), since the stress components in steady shear flow can be measured more easily than the complex modulus is, and the limit of Eq. (5b) converges more rapidly than that of Eq. (5a) does. This rapid convergence of the limit of Eq. (5b) follows from the fact that  $(-\partial P/\partial \ln r)/\kappa^2$  and  $\sigma_{12}/\kappa$  remain constant up to high values of  $\kappa$  for usual polymer solutions, compared with that  $G'/\omega^2$  and  $G''/\omega$  begin to deviate from constant at a relatively low value of  $\omega$ <sup>12</sup>. Therefore  $J_e$  was here mainly evaluated from the steady flow data. Dynamic method was applied only to those solutions with high viscosity for which the normal stress measurement was difficult.

## Materials

The systems used for measurements were polystyrene solutions in toluene (Tol), dioctyl phthalate (DOP) and Kaneclor 400 (K) with various combinations of the molecular weight and concentration.

Two types of polystyrene samples were used; thermal polystyrenes and a living polystyrene. The thermal polystyrenes were synthesized through the thermal polymerization at various temperatures. The conversion was suppressed under 10% if possible, in order to avoid chain branching. However, polymerization rate at high temperatures ( $>130^\circ\text{C}$ ) was so rapid that the conversion could not be kept at a low level, and the samples polymerized at these high temperatures may contain some branches in molecule. Viscosity average molecular weights of the thermal polystyrenes were determined by

$$[\eta] = 1.13 \times 10^{-6} M_v^{0.73} \text{ (Benzene, } 25^\circ\text{C)} \quad (7)$$

The molecular weights are summarized in Table 1. The number following T in the name of samples, e.g. T40, indicates the temperature in centigrade at which the sample was synthesized. Although the sample T130 was polymerized at  $130^\circ\text{C}$  in an air bath, its low molecular weight suggests that the temperature in the reaction vessel was probably much higher. Other samples were synthesized in

Table 1. Polystyrene Samples.

Sample	Conversion %	$M \times 10^{-5}$
T40	7.3	25.1
T60	8.6	19.5
T80	8.5	10.4
T95	10.7	7.2
T115	5.1	5.6
T130	high	0.50
T145	65	1.82
T160	85	0.63
T190	77	0.33
14 a	—	18.0

water bath or oil bath of the indicated temperature, so that no trouble concerning the reaction temperature seems to be involved.

The living polystyrene, 14a, was supplied from Pressure Chemical Co. According to the data sheet attached to the sample, the sample has a sharp distribution of molecular weight, *i.e.*  $M_w/M_n \leq 1.25$ . The living polystyrene was dissolved in benzene and precipitated in methanol. This procedure was repeated several times in order to remove low molecular weight fraction which often contaminates a living polystyrene. The viscosity average molecular weight determined by Eq. (7) is in agreement with the weight average molecular weight given in the data sheet.

Two solvents, toluene and dioctyl phthalate, were supplied from Nakarai Chemicals Co. and were used without further purification. Another solvent, Kaneclor 400, was a mixture of chlorinated diphenyl and polyphenyl from Kanegafuchi Chemical Ind. Viscosities of these solvents, Tol, DOP and K, were  $5.2 \times 10^{-3}$ ,  $3.5 \times 10^{-1}$  and 1.4 poise at 30°C, respectively. Use of the viscous solvents, DOP and K, were necessary for the normal stress measurements of solutions of low molecular-weight polymers. The used combinations of molecular weight, concentration and solvent are shown in Table 2.

Table 2. Steady Shear Compliance and Viscosity of Concentrated Polystyrene Solutions at 30°C.

Sample	solvent	conc.(g/dl)	method*	$\eta$ (poise)	$J_e \times 10^4(\text{cm}^2/\text{dyne})$
T40	Tol	13.3	D	$2.25 \times 10^3$	3.2
		8.8	D	$1.03 \times 10^3$	8.9
		6.2	D	$2.10 \times 10^1$	15.9
T60		13.3	S	$5.2 \times 10^2$	3.1
T80		17.8	D	$2.70 \times 10^2$	1.50
		13.3	S	$4.7 \times 10^1$	3.1
		8.8	S	$8.0 \times 10^0$	8.2
T95		17.8	D	$5.8 \times 10^1$	2.0
		13.3	S	$1.40 \times 10^1$	3.8
T115		13.3	S	$6.8 \times 10^0$	3.8

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T145	DOP	15.0	S	$1.10 \times 10^2$	1.47
T160	DOP	15.0	S	$1.85 \times 10^1$	1.04
T130	DOP	30.0	S	$5.00 \times 10^2$	0.48
		25.0	S	$1.30 \times 10^2$	0.78
		20.0	S	$4.4 \times 10^1$	1.32
		15.0	S	$1.35 \times 10^1$	2.0
		12.5	S	$7.8 \times 10^0$	1.67
T190	K	25.0	S	$6.2 \times 10^2$	0.50
		20.0	S	$1.90 \times 10^2$	0.67
		15.2	S	$6.4 \times 10^1$	0.78
		12.0	S	$3.4 \times 10^1$	0.84
14 a	Tol	17.8	S	$1.00 \times 10^3$	1.35
		15.6	S	$5.3 \times 10^2$	1.37
		13.3	S	$2.5 \times 10^2$	1.44
		8.8	S	$2.6 \times 10^1$	3.84
		6.6	S	$8.0 \times 10^0$	6.89

\* D and S imply that  $\eta$  and  $J_e$  are obtained from the complex modulus and from the stresses in steady shear flow, respectively.

## RESULTS AND DISCUSSIONS

### Results

In Fig. 1 are shown the real and imaginary parts of the complex modulus,  $G'$  and  $G''$ , obtained for solutions of PS (T40) in toluene with various concentrations.

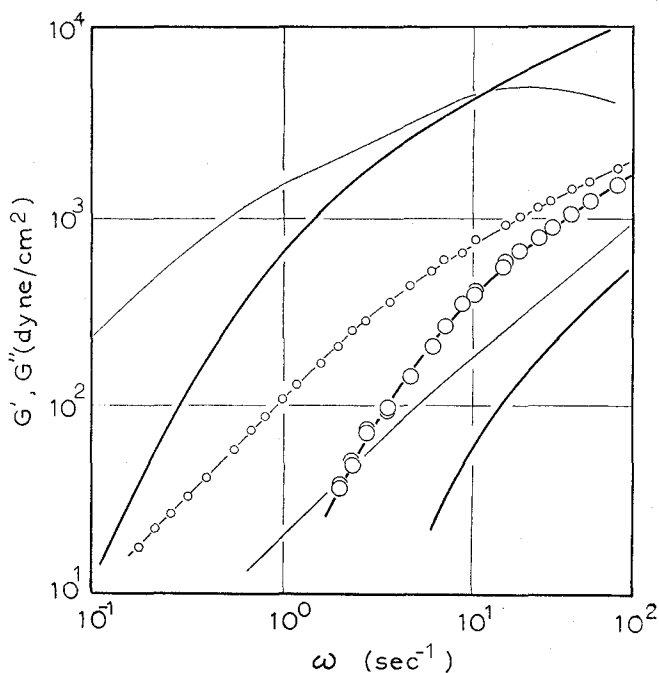


Fig. 1. The real part  $G'$  and the imaginary part  $G''$  of the complex modulus for solutions of PS-T40 in toluene with various concentrations at 30°C. Thick lines represent  $G'$  and thin lines  $G''$ . Concentrations are 13.3, 8.8 and 6.2 g/dl from left to right. Raw values of  $G'$  and  $G''$  are shown only for 8.8 g/dl-solution.

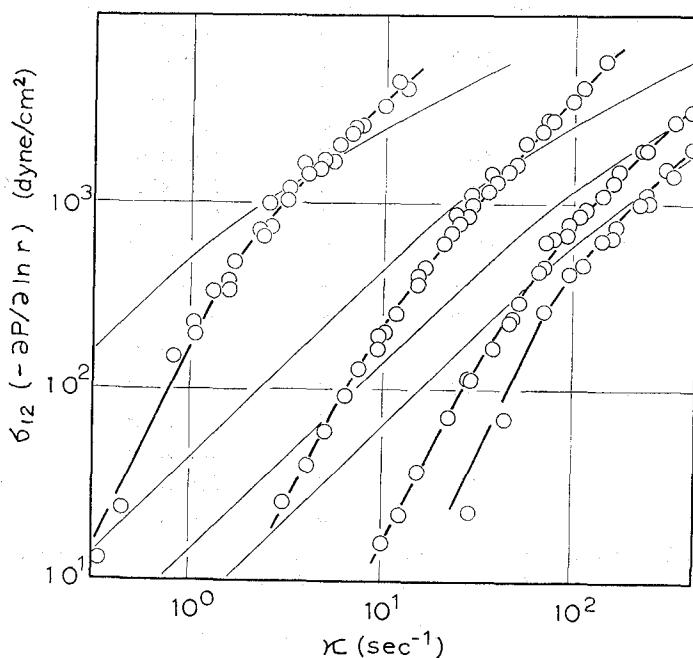


Fig. 2. The normal stress  $(-\partial P/\partial \ln r)$  and the shear stress  $\sigma_{12}$  for 13.3 g/dl-solutions in toluene of polystyrene with various molecular weights at 30°C. Circles represent  $(-\partial P/\partial \ln r)$  and the thin lines  $\sigma_{12}$ . The molecular weights of PS are  $2.51 \times 10^6$ ,  $1.95 \times 10^6$ ,  $1.04 \times 10^6$ ,  $7.2 \times 10^5$  and  $5.6 \times 10^5$  from left to right.

Figure 2 shows the normal pressure gradient  $(-\partial P/\partial \ln r)$  and the shear stress  $\sigma_{12}$  obtained for 15% solutions of thermal polystyrenes with various molecular weights in toluene. It is obvious from Figs. 1 and 2 that at small  $\omega$  or  $\kappa$ , the quantities  $G'$  and  $G''$  are proportional to  $\omega^2$  and  $\omega$ , respectively, and the quantities  $(-\partial P/\partial \ln r)$  and  $\sigma_{12}$  to  $\kappa^2$  and  $\kappa$ , respectively. Thus, using Eqs. (5a) and (5b), we can readily evaluate the steady shear compliance  $J_e$ . The values of  $J_e$  thus obtained are shown in Table 2 together with the values of the zero-shear viscosity  $\eta$ . The similar measurements of  $J_e$  and  $\eta$  were performed for various combinations of solvent, concentration and molecular weight. The results are summarized in Table 2, though the plots of the dynamic modulus and normal stress against  $\omega$  and  $\kappa$  are not reproduced here. In this table, the method employed for evaluation of  $J_e$  was indicated by the symbol S and D: S indicates that  $J_e$  was evaluated from the steady flow data with the aid of Eq. (5b), and D indicates that  $J_e$  was evaluated from the dynamic mechanical data with the aid of Eq. (5a).

#### Dependence of $J_e$ on $M$ and $c$

In order to see the dependence of  $J_e$  on the molecular weight  $M$  and concentration  $c$ , the values of  $J_e$  for various series of solutions are plotted against  $M$  and  $c$  in Figs. 3 and 4. In Fig. 3 are plotted the values of  $J_e$  for 15% (13.3 g/dl) solutions of thermal polystyrenes with high molecular weight in toluene and for 15 g/dl solutions of thermal polystyrenes with low molecular weight in dioctylphthalate and Kaneclor. Here the term "high" or "low" used for the molecular weight indicates that the solution is composed of the polymers with  $M$  higher or

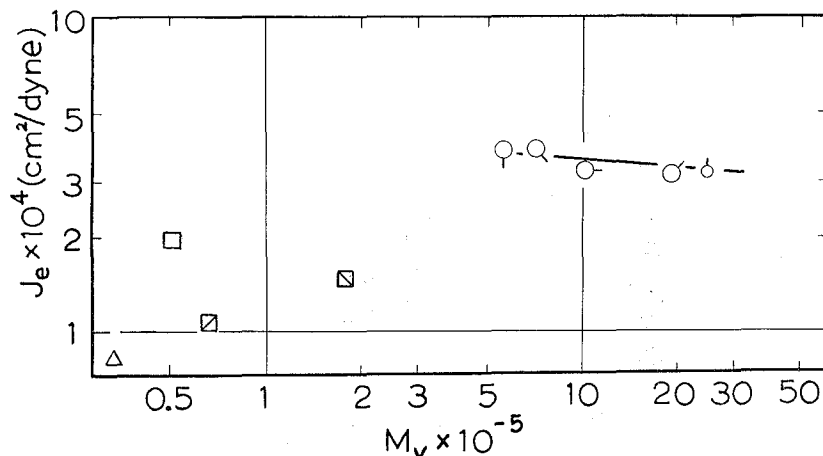


Fig. 3. The steady shear compliance  $J_e$  of polystyrene solutions as functions of the molecular weight. Temperature, 30°C. Circles with pips represent the result obtained for 15% (13.3 g/dl) solutions in toluene. One small circle represents the data obtained from the dynamic mechanical method, and the large circles represent those obtained from the steady flow method. Direction of the pips represents the molecular weight; pip up,  $M_v = 2.51 \times 10^6$ ; successive 45° rotation clockwise,  $1.95 \times 10^6$ ,  $7.2 \times 10^5$  and  $5.6 \times 10^5$ , respectively. Meaning of other marks are:  $\triangle$ , 15 g/dl in Kaneclor with  $M_v = 3.3 \times 10^4$ ;  $\square$ ,  $\boxtimes$  and  $\boxminus$ , 15 g/dl in DOP with  $M_v = 5.0 \times 10^4$ ,  $6.3 \times 10^4$  and  $1.82 \times 10^5$ , respectively.

lower than  $M_c$  which is estimated by Eq. (1). As readily seen from the figure, the quantity  $J_e$  was independent of  $M$  in the solutions of high molecular weight polystyrenes. On the other hand, in the solutions of low molecular weight polystyrenes, such a definite dependence of  $J_e$  on  $M$  can not be determined because of scattering of the data. We can see only that  $J_e$  increases slightly with increasing  $M$ .

In Fig. 4, we show the concentration dependence of  $J_e$  in the systems, T40, T80 and 14a in toluene, T130 in dioctylphthalate and T190 in Kaneclor. Here the solutions of T40, T80 and 14a can be classified as the systems with high molecular weight ( $M > M_c$ ) and the solutions of T130 and T190 as those with low molecular weight ( $M < M_c$ ). Here  $M_c$  was evaluated from Eq. (1). Values of  $J_e$  for the solutions of high molecular-weight polystyrenes are aligned on the straight lines with slope of  $-2$  in the plot of  $\log J_e$  vs.  $\log c$ . (See, line A for T40 and T80, and line B for 14a) Therefore it is concluded that  $J_e$  is inversely proportional to  $c^2$  in solutions of high molecular-weight polystyrenes. In solutions of low molecular-weight polystyrene ( $M < M_c$ ), concentration dependence of  $J_e$  seems to vary with varying molecular weight. In the solutions of T130 in DOP, in which  $M$  is not much lower than  $M_c$ , values of  $J_e$  were located only slightly lower than the extension of the line A. On the other hand, values of  $J_e$  for T190 solutions in Kaneclor, for which  $M$  is sufficiently lower than  $M_c$ , were located far below the extension of line A, and they were less sensitive to concentration than those for T130 solutions were. The  $\log J_e$  vs.  $\log c$  plots of these systems with  $M < M_c$  can not be represented by straight lines but by curved lines C and D. If the concentration dependence of  $J_e$  are expressed in a power type equation,  $J_e \propto c^{-n}$ , the exponent  $n$  is approximately two for T130 solutions and approximately unity for



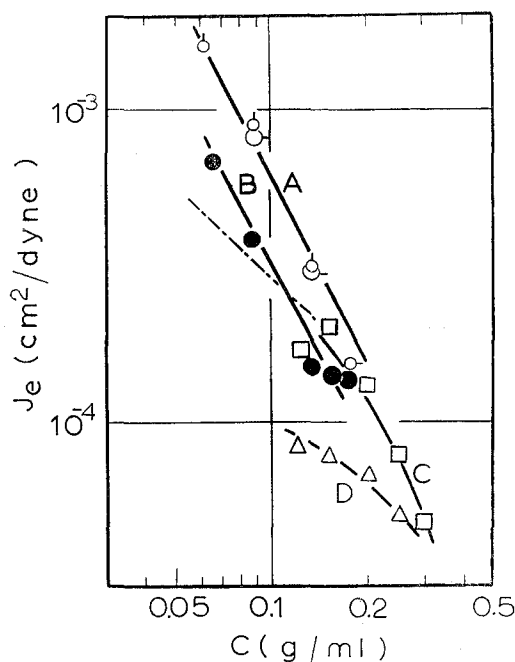


Fig. 4. The steady shear compliance  $J_e$  of polystyrene solutions as functions of the concentration  $c$ . Temperature, 30°C. The meaning of marks are the same as in Fig. 3, except for black circles representing the result for PS-14a solution in toluene. The solid lines A and B are straight lines with slope  $-2$ . The chain line illustrates the theoretical value of  $J_e$  for the sample 14a calculated by the modified Rouse theory.

T190 solutions, though it decreases with decreasing concentration.

Above observations are summarized as follows. In solutions of high molecular-weight polystyrenes,  $J_e$  is independent of  $M$  and is inversely proportional to  $c^2$ . This type of concentration dependence seems to be valid irrespective of the molecular weight distribution of polymers. In these solutions of high molecular-weight polystyrenes, the experimental values of  $J_e$  can be given as

$$J_e = 6 \times 10^{-6} c^{-2} \text{ (thermal polystyrene)} \quad (8a)$$

$$= 3 \times 10^{-6} c^{-2} \text{ (living polystyrene)} \quad (8b)$$

Here  $J_e$  is expressed in unit of  $\text{dyne}^{-1} \cdot \text{cm}^2$  and  $c$  in unit of g/ml. Curiously,  $J_e$  is sensitive to the distribution of molecular weight, although it is insensitive to the molecular weight itself.

In the case of lower molecular-weight polymers, the dependence of  $J_e$  on  $M$  and  $c$  is more complicated. In the solutions of T130 in DOP, for example, the values of  $J_e$  at various concentrations are not much different from those calculated from Eq. (8a) (see Fig. 4), although these solutions lie in the range  $M > M_c$ . Thus  $J_e$  in the system with the molecular weight slightly lower than  $M_c$  is essentially the same as that in highly entangled systems. On the other hand,  $J_e$  in solutions of very low molecular-weight polystyrene T190 in Kaneclor is roughly proportional to  $c^{-1}$ , and is much lower in magnitude and less sensitive to the concentration than the value calculated from Eq. (8a) is. A slight increase of  $J_e$  with increasing

molecular weight is observed in solutions of very low molecular-weight polystyrenes in Fig. 3. Thus, the values of  $J_e$  for the systems with  $M < M_e$  are tentatively written as,

$$J_e \propto M^\alpha / c^\beta \quad 0 < \alpha < 1, 1 < \beta < 2, \quad (9)$$

in which  $\alpha$  decreases and  $\beta$  increases if the molecular weight of the system approaches  $M_e$ .

### Comparison of Results with Theories

The results described above will be compared with the theories referred to at the beginning of this paper. We first note that the empirical relation, (8b), obtained for the living polystyrene 14a conflicts with the prediction by the modified Rouse theory, Eq. (2). Nevertheless the values of  $J_e$  calculated by Eq. (2) comes very close to the observed ones. The chain line in Fig. 4 shows the calculated values of  $J_e$  for the sample 14a ( $M = 1.8 \times 10^6$ ). The calculated and observed value of  $J_e$  lie quite close to each other at concentration of about 0.1 g/ml. This result may lead to a misleading conclusion that the modified Rouse theory is applicable to this system, if  $J_e$  is measured only at one concentration near 0.1 g/ml.

If Hayashi's theory is applied to the analysis of the results, Eq. (3b) must be equated to the empirical equation (8b).

$$M_e c = 6.6 \times 10^4 \quad (10)$$

This value of  $M_e$  is about 60% higher than that appeared in Eq. (1). In spite of this discrepancy, it may be concluded that Hayashi's theory describes fairly well the flow behavior of polymer solutions containing entanglement couplings.

For solutions of low molecular-weight polystyrene, the observed values of  $J_e$  can be described by Eq. (9), where  $\alpha$  and  $\beta$  approach unity as  $c$  or  $M$  decreases. At first sight, this result leads to a thought that the modified Rouse theory is applicable to the systems with very low molecular weight. However, the observed values of  $J_e$  for the solutions of T190 are about 20 times as large as those calculated by Eq. (2). This discrepancy is too large to be interpreted by the polydispersity of the molecular weight of the polymer. Thus the dependence of  $J_e$  on  $M$  and  $c$  for systems with a very low molecular weight can not be described by the modified Rouse theory nor by Hayashi's theory. Further development of molecular theory is clearly needed. Finally, we note that the dependence of  $J_e$  on  $M$  and  $c$  does not change abruptly at the molecular weight  $M_e$  in contrast to the dependence of  $\eta$  on  $M$  and  $c$ . This fact seems to imply that one entanglement point per molecule on an average is sufficient to affect the steady shear compliance but not the viscosity.

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